Supporting Information (SI) for:

Reaction mechanism and kinetics for ammonia synthesis on the Fe(111) Surface

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1. Comparison with PBE results

This paper used the DFT/PBE functional including the Grimme empirical correction for London dispersion (van der Waals attraction) because this level of DFT in our recent calculations of ORR for Pt and CO2RR for Cu led to very close agreement with experiment (barriers to 0.05 eV and overpotentials to 0.05 V). However, we also carried out all calculation using just PBE with no D3 corrections (often the case for metallic systems). These calculations used the PBE optimized lattice parameters for Fe (PBE: a=2.827 Å, PBE-D3: a=2.807 Å, experiment at 300K a=2.867 Å, and experiment at 673K: a=2.881 Å).

Figure S1 shows the new energetics for PBE corresponding to Fig. 2 in the text.

Using these modified energetics, we carried out the full set of kMC simulations, leading to Table S1, in place of Table 2 of the main text. For Somorjai conditions (673K) this predicts a TOF=89.3 compared to 17.7 for PBE-D3 and 9.7 experiment. This indicates that simple PBE may lead to rates that are too fast.

In particular, the poisoning effect of ammonia is substantially underestimated with PBE, with only a modest decrease of NH_3 production by increasing ammonia pressure. Thus

- the TOF changes from 89.3 to 75.7 NH_3mol/s/(2x2)surface area as the NH_3 pressure is increased from 1.5 torr to 1 atm at T=673 K, pH_2=15 atm, pN_2=5 atm; In contrast for PBE-D3, the TOF changes from 17.7 to 2.8 NH_3mol/s/(2x2)surface area. The experiments by Somorjai suggest a change by a factor of ~3 from 1.5 torr to 20 torr.
- the TOF increases from 1983.5 to 1430.0 NH_3mol/s/(2x2) at T=730 K as conditions are changed from pH_2=150 atm, pN_2=50 atm, pNH_3=1 atm, to pH_2=120 atm, pN_2=40 atm, pNH_3=20 atm. In contrast for PBE-D3, the TOF changes from 93.7 to 18.6.
- However, the increase of ammonia production with temperature seems to be better predicted by PBE: from TOF=89.3 to 231.2 NH_3mol/s/(2x2) as the temperature is increased from 673 K to 730 K, under condition of pH_2=15 atm, pN_2=5 atm, pNH_3=1.5 torr. In contrast for PBE-D3, the TOF changes from 17.7 to 83.3. The experiments by Somorjai suggest a change by a factor of 2.4.

Overall, we conclude that theGrimme D3 dispersion correction with the Becke-Johnson parameters lead to a better description of the reaction energetics.

Table S1 lists the steady-state apparent ΔG (i.e., the logarithm of the relative populations) for the most important states obtained using PBE results in the kMC.

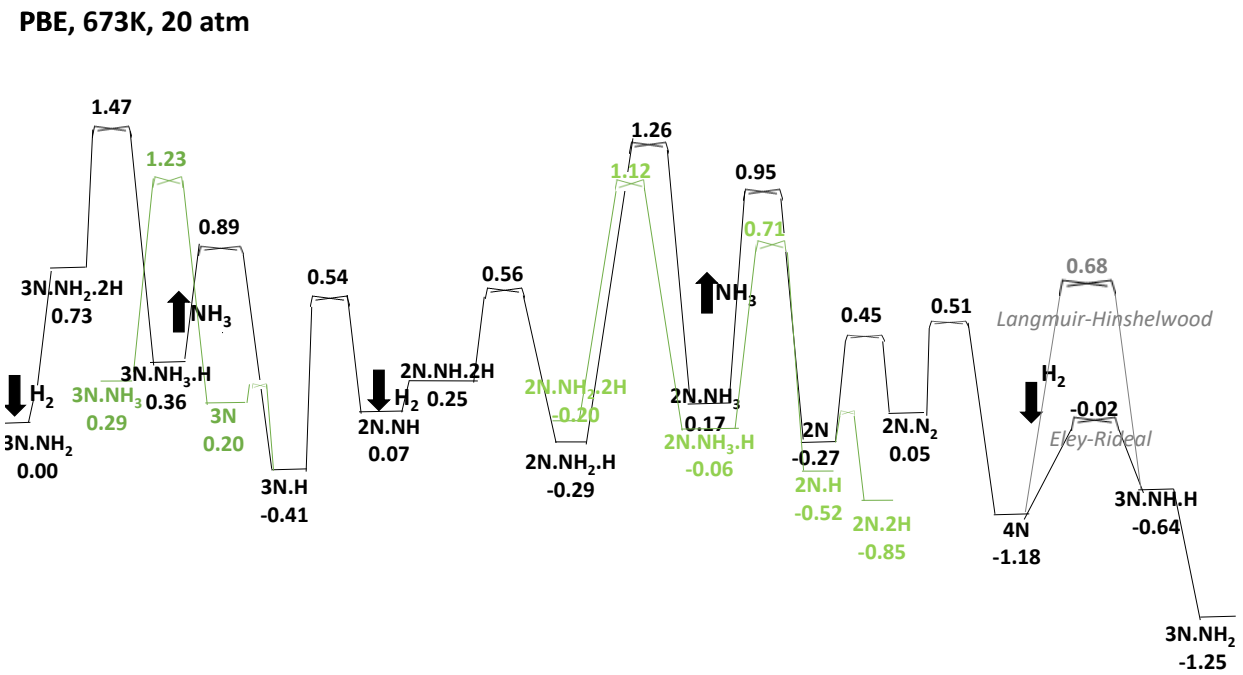


Fig S1. This is equivalent to Fig. 2 of the text except using PBE rather than PBE-D3. We also use the PBE lattice parameter for bulk Fe. Energy landscape for NH_3 synthesis reactions under

Somorjai condition, 673 ºK, 20atm. The lowest energy state $3N\_NH_2$ is taken as reference, with a free energy of zero. We considered the linear pathway in black and proposed alternative pathway in green, in order to lower some barriers. NH_3 production rate is dominated by 3 steps: N_2 adsorption, hydrogenation of NH_2, and NH_3 desorption. Note that we consider reacting 3 H_2 plus 1 N_2 to form 2 NH_3, so that the total free energy decreases by 1.25 eV as we go from $3N\_NH_2$ on the left to $3N\_NH_2$ on the right.

	T=673, pH_2=15, pN_2=5, pNH_3=1.5/760			T=730, pH_2=150, pN_2=50, pNH_3= 1			T=730, pH_2=120, pN_2=40, pNH_3=20		
configuration	t_i (%)	- $\ln(P_i/P_0)$	ΔG	t_i (%)	- $\ln(P_i/P_0)$	ΔG	t_i (%)	- $\ln(P_i/P_0)$	ΔG
3N_NH_2	32.7	0.00	0.00	29.7	0.00	0.00	38.4	0.00	0.00
3N_NH_2_2H	1E-4	0.73	0.73	7E-4	0.67	0.66	8E-4	0.68	0.68
3N_NH_3_H	8E-5	0.75	0.36	6E-3	0.53	0.27	0.14	0.35	0.29
3N_H	39.9	-0.01	-0.05	15.1	0.04	-0.22	16.8	0.05	-0.02
2N_NH	2E-2	0.43	0.43	1E-2	0.48	0.26	2E-2	0.49	0.46
2N_NH_2H	9E-4	0.61	0.61	3E-3	0.58	0.36	3E-3	0.60	0.58
2N_NH_2_H	10.7	0.06	0.07	18.1	0.03	-0.19	16.3	0.05	0.03
2N_NH_3	1E-4	0.73	0.53	6E-4	0.68	0.26	3E-3	0.60	0.48
2N	4E-4	0.65	0.45	8E-4	0.66	0.11	7E-4	0.69	0.51
4N	2.95	0.14	-0.46	0.73	0.23	-0.86	1.15	0.22	-0.86
3N_NH_H	1E-3	0.60	0.08	2E-3	0.60	-0.41	3E-3	0.60	-0.39
2N_2H_lin	9.4	0.07	-0.13	23.8	0.01	-0.56	17.4	0.05	-0.16
2N_2H	2.0	0.16	-0.04	4.15	0.12	-0.43	3.0	0.16	-0.03
2N_NH_3_H	1E-3	0.60	0.45	1E-2	0.49	-0.02	0.11	0.37	0.20
2N_H	3E-2	0.40	0.49	1E-1	0.36	-0.19	8E-2	0.39	0.21
2N_NH_2_2H	2.3	0.15	0.16	8.18	0.08	-0.14	6.6	0.11	0.10
kMC NH_3 mol/s/(2x2)	89.3			1983.5			1430.0		
total NH_3mol	148584			193826			172003		
3N_NH_3_H ↔ 3N_H	74312			96935			86021		
2N_NH_3_H ↔ 2N_H	74272			96891			85982		

Table S1. Kinetic Monte Carlo results based on PBE DFT (without the D3 London dispersion correction). For Somorjai conditions (673K) this predicts a TOF=89.3 compared to 17.7 for PBE-D3 and 9.7 experiment. Top rows – Per cent of populations (i.e., residence times) = t_i(%), apparent free energy differences [evaluated as minus the logarithm of ratio of populations = P_i/P_0, where P_0 = P_{3N_NH2}], and thermodynamic free energy differences (ΔG) for selected configurations in a Fe(111)-(2x2) unit cell under steady-state of ammonia synthesis as predicted by kMC simulations at different temperatures (673 and 730 K), and different H_2, N_2, NH_3 pressures, using DFT/PBE data instead of DFT/PBE-D3 data as in Table 2 of the main text. All configurations are assumed in the zig-zag arrangement, except for "2N_2H_lin" which is linear (see SI for details). Temperature in Kelvin, pressure in atmospheres, free energy differences in eV. Bottom rows – NH_3 molecules produced per second per (2x2) unit cell under the given conditions [NH_3mol/s/(2x2)], total number of NH_3 molecules produced in the kMC runs (total

NH_3mol), further partitioned into the 2 main steps involving NH_3 adsorption/desorption: $3N\_NH_3\_H \leftrightarrow 3N\_H$; $2N\_NH_3\_H \leftrightarrow 2N\_H$

2. Transition state geometry and potential energy curves

The Transition state geometries and potential energy curves are reported in Fig. S2-S4

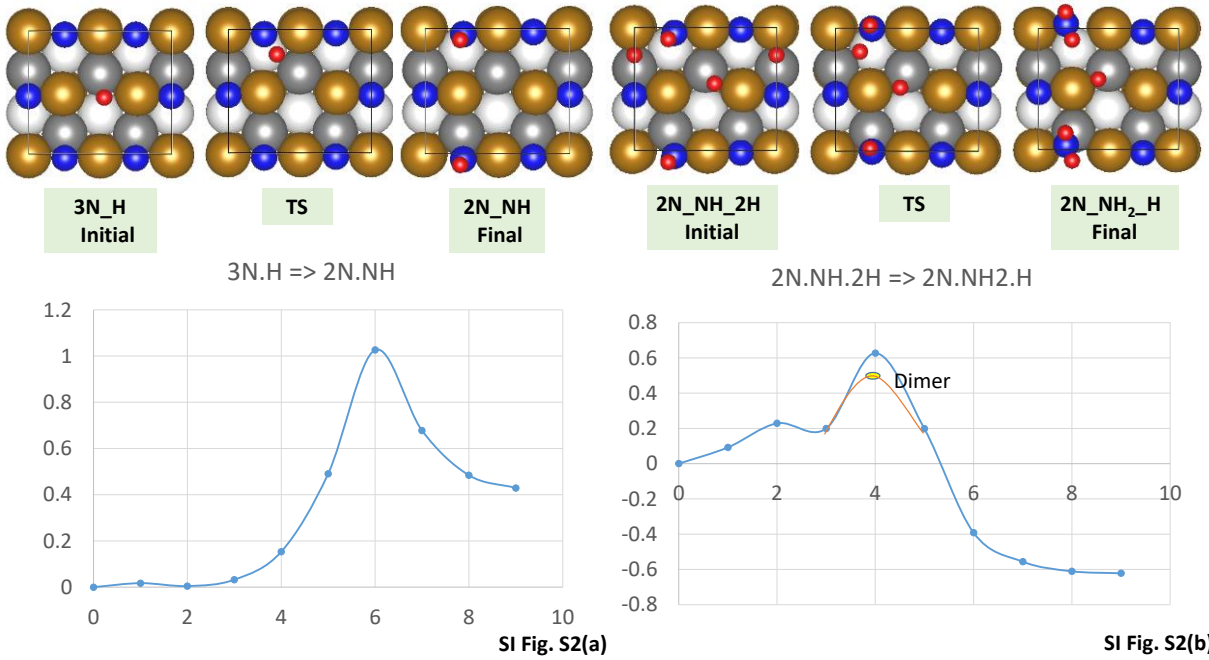


Fig. S2. Mechanism for 3N_H =>2N_NH, migration of hydrogen and addition to N on the surface (LH) is shown in a). Mechanism for 2N_NH_2H => $2N\_NH_2\_H$, hydrogen migration and addition to NH on the surface (LH) is shown in b). The climbing NEB method generates a true transition state, as we confirmed by performing vibrational frequency calculations showing a single negative curvature in the Hessian. The dimer calculations were performed if the negative frequency was found from NEB transition state image.

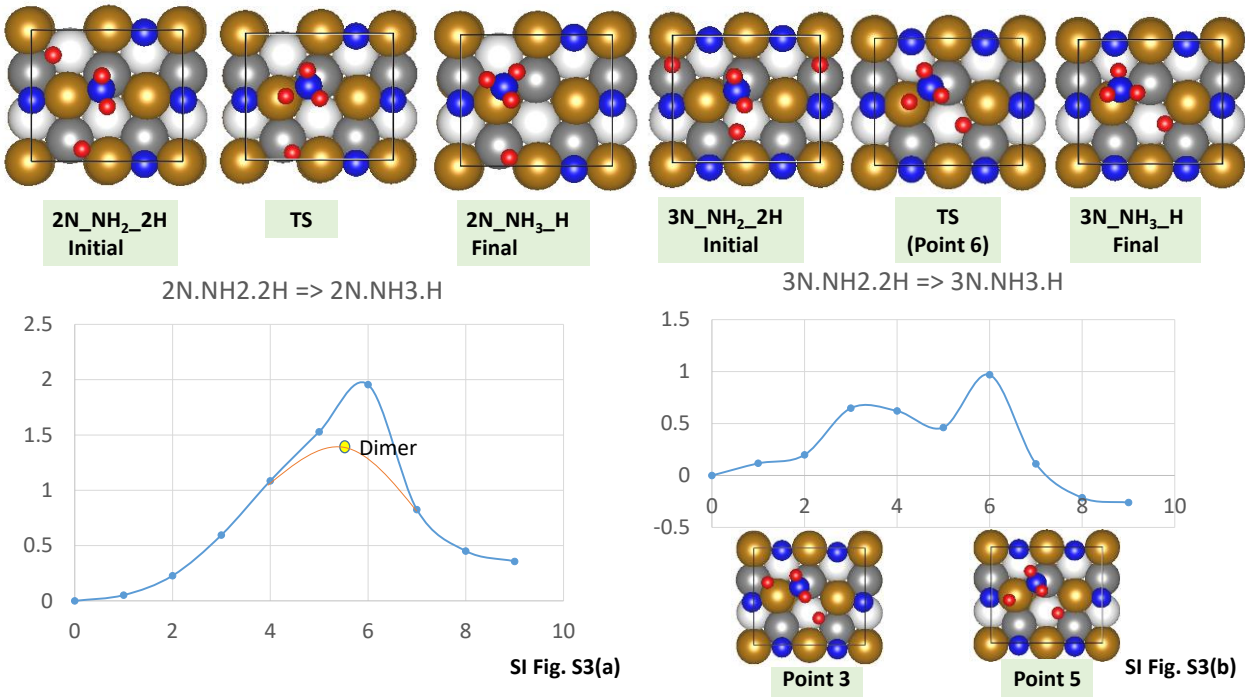
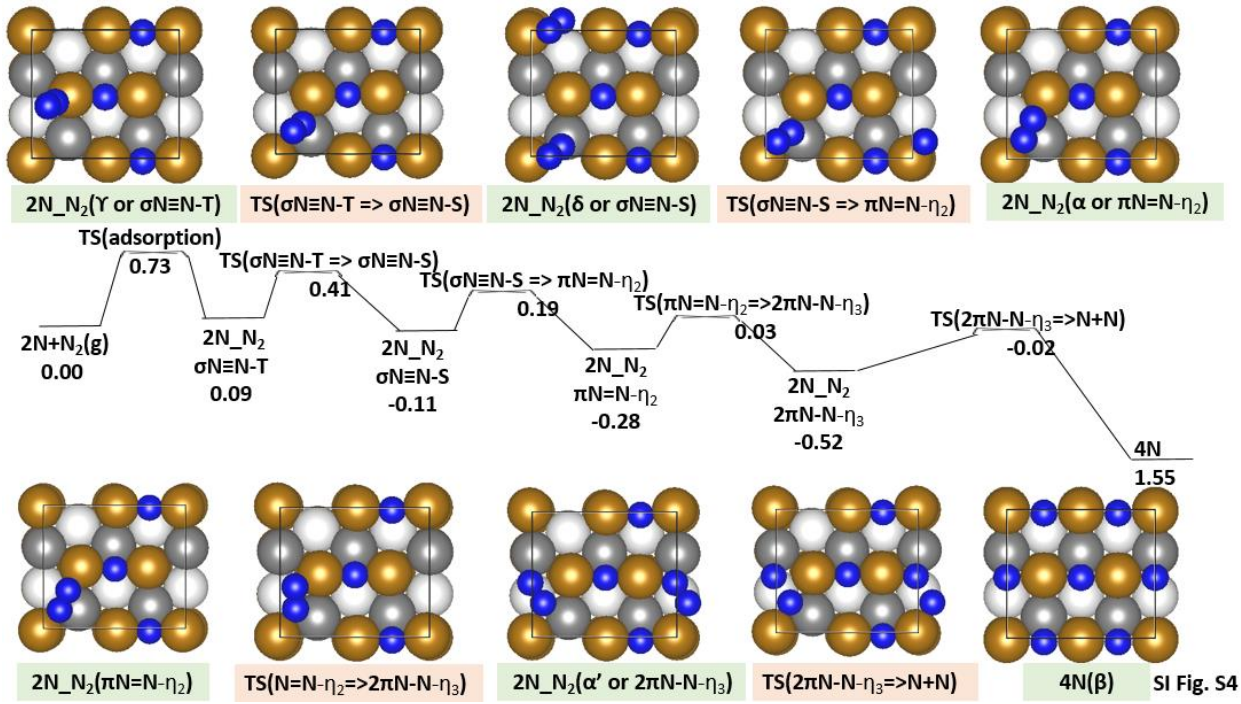


Fig S3. Mechanism for 3N_NH_2_2H => 3N_NH_3_H, hydrogen migration and addition to NH_2 on the surface (LH) is shown in a). Mechanism for 2N_NH_2_2H => 2N_NH_3_H, hydrogen migration and addition to NH_2 on the surface (LH) is shown in b). The climbing NEB method generates a true transition state, as we confirmed by performing vibrational frequency calculations showing a single negative curvature in the Hessian. The dimer calculations were performed if the negative frequency was found from NEB transition state image.



SI Fig. S4

Fig S4. Mechanism for N_2 dissociation is purposed to be triple-bonded N_2 adsorbed on the first layer (denoted as N^3N-T phase, the superscription in the middle represents the bond order, and T represents adsorption on top layer) => triple-bonded N_2 adsorbed on the second layer (denoted as N^3N-S phase) => double-bonded N_2 on two-fold site (denoted as N^2N-η_2 phase) => single-bonded N_2 on three-fold site (denoted as N^1N-η_3 phase) => dissociative 4N.

3. Linear versus zig-zag configurations

For each stoichiometry of the system, there can be more than one possible configuration. Thus consider the 4 bridge sites of the (2x2) unit cell. If 2 or more different species are adsorbed on these, sites there can be at least two alternative configurations, which we name "linear" and "zig-zag", as illustrated in Figure S5 for the "2N" system. Indeed, for most stoichiometries the "linear" configuration is lower in energy than the "zig-zag" one, but only the "2N zig-zag" configuration is able to dissociate N_2. Thus most of our discussions report only zig-zag configurations. An exception is for "2N_2H_lin" which is linear and is reported in Table 2 and Table S1 due to its abundance (high population) under steady state conditions.

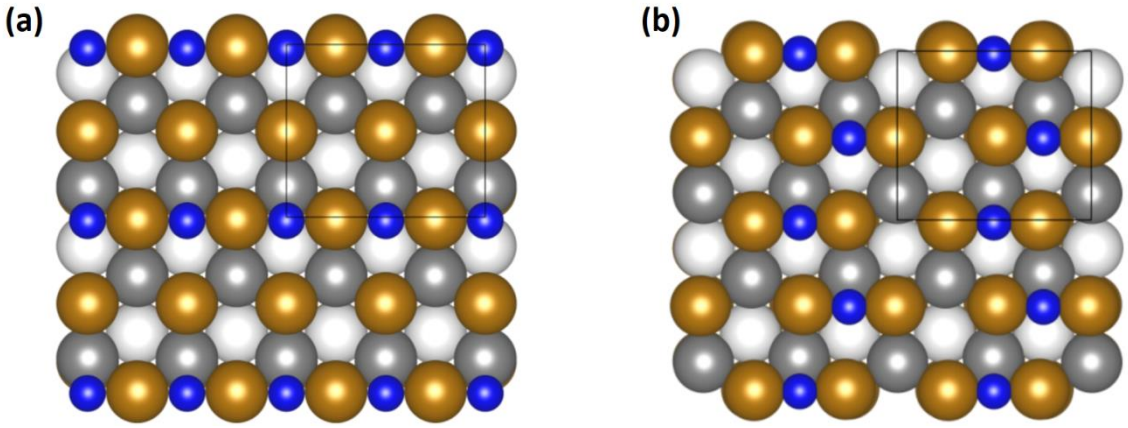


Figure S5. Schematic illustration of: (a) "linear" and (b) "zig-zag" configurations for the "2N" system. The (2x2) unit cell is replicated 4 time for better visualization.

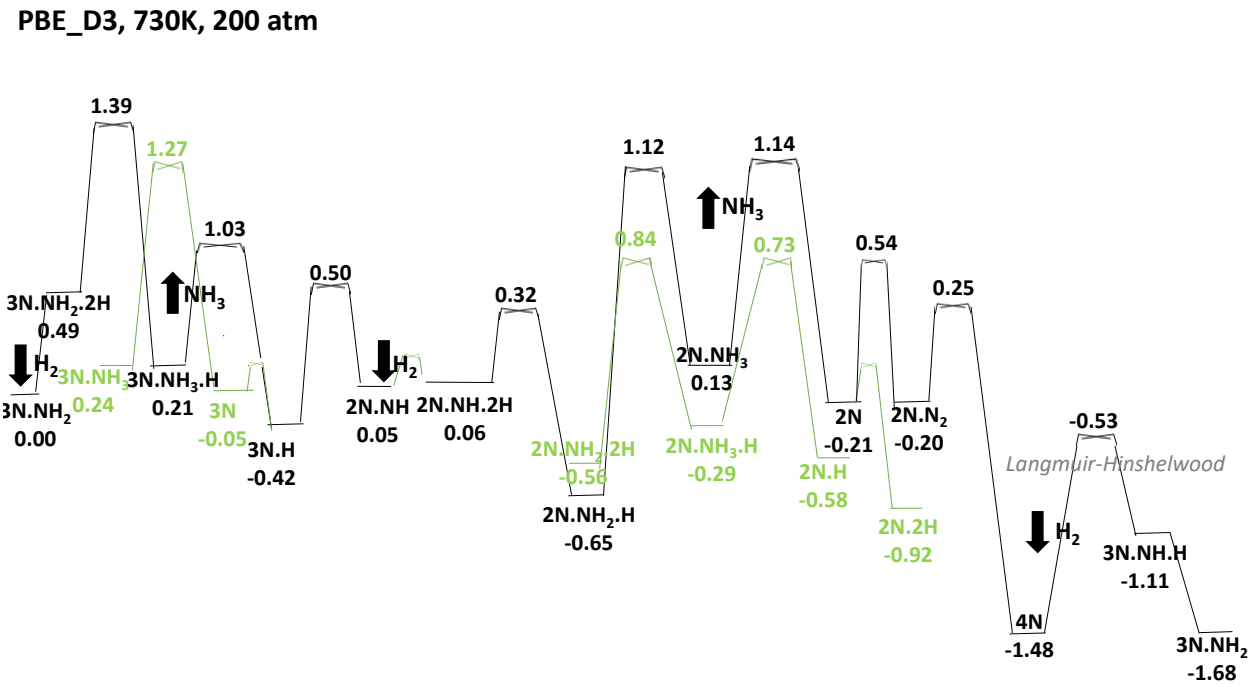


Fig S6. This is equivalent to Fig. 2 of the text except using 730K , 200 atm instead of 673K, 20 atm. The lowest energy state 3N_NH_2 is taken as reference, with a free energy of zero. We considered the linear pathway in black and proposed alternative pathway in green. NH_3 production rate is dominated by 3 steps: N_2 adsorption, hydrogenation of NH_2, and NH_3 desorption. Note that we consider reacting 3 H_2 plus 1 N_2 to form 2 NH_3, so that the total free energy decreases by 1.68 eV as we go from 3N_NH_2 on the left to 3N_NH_2 on the right.

2. Comparison with previous theory results

Table S2 compares our DFT calculations with previous published values

States	Description	rN-N	Ead (present)	covergae (present)	Norskov	coverage (Noskov)	Lin	coverage (Lin)
γ	top vertical (1st layer)	1.13	-0.62	0.25	-0.400	1.00	NA	NA
δ	top vertical (2nd layer)	1.16	-0.72	0.25	-0.150	1.00	NA	NA
α	2-fold site	1.20	-0.84	0.25	-0.500	1.00	NA	NA
α'	3-fold site	1.33	-0.67	0.25	-0.250	1.00	NA	NA
β	dissociated N	4.02	-1.56	0.25	-1.400	1.00	-1.696	0.33
NH	TTS site	NA	-4.59	0.25	NA	NA	-4.182	0.33
NH2	TS site	NA	-3.31	0.25	NA	NA	-2.811	0.33
NH3	T site	NA	-0.93	0.25	NA	NA	-0.705	0.33

Table S2 Comparison of dissociatively chemisorbed binding energies for N_2, with Mortensen et al.[50] Different adsorption states are labeled as α, β, γ. Comparison of different chemisorbed species binding energies with Lin et.al.[41]

5. Instructions on excel file containing full numerical data

5.1 Overview

Excel sheet "HB_111_Apr24" contains all calculations mentioned in this paper.

It is divided into 4 sub-sheets, namely

- "ENERGY_COMPILE_673K",

This sheet has two complete sets of 53 intermediate states' energy using PBE and PBE-D3 functionals at 673 K, Somorjai condition.

- "ENERGY_COMPILE_730K",

This sheet has two complete sets of 53 intermediate states' energy using PBE and PBE-D3 functionals at 730 K, industrial condition.

- "Small Molecule",

This sheet has two sets of molecular energy using PBE and PBE-D3 functionals at both 673 K and 730 K,

- "Reaction_Barriers",

This sheet has NEB electronic energy of all crucial reaction barriers along the NH_3 production pathway.

5.2 Detailed Explanation and Instruction

"ENERGY_COMPILE_673K" and "ENERGY_COMPILE_730K" are parallel of each other, and we have the relative energy in Column J and M to plot Figure 2 in the text, Figure S1 and S6 in SI. Both sheets read data from "Small Molecule" and "Reaction_Barriers" because free energy is dependent upon temperature and pressure.

Currently, "ENERGY_COMPILE_673K" reflects Somorjai experiment condition: 15 atm pressure for H_2, 5 atm for N_2 and 1.5 torr for NH_3. Electronic energy of these small molecules and 53 intermediate states (column H and K) were calculated from VASP, and they are independent of pressure and temperature. On the other hand, free energy (column I and L) depends on temperature and pressure, thus need to be carefully selected from "Small Molecule" and "Reaction_Barriers". Column J and M are dG calculated using PBE and PBE-D3 functionals respectively, and they are referenced to the lowest energy state $3N.NH_2$. Each time 1 NH_3 is produced, we subtracted the free energy of ammonia. Column H-J are PBE values using PBE lattice parameter 2.820 Å, Column K-M are PBE-D3 values using PBE_D3 lattice parameter 2.807 Å. We have also considered using experiment lattice parameter of iron at 673K, which is 2.881 Å, from Column N to P, and they give very similar answers to PBE-D3 lattice parameter results (Column K-M), within ~0.1 eV in difference.

Similarly, "ENERGY_COMPILE_730K" reflects industrial condition of producing NH_3: 150 atm pressure for H_2, 50 atm for N_2 and 1.5 torr for NH_3. The layout of this sheet is exactly the same as "ENERGY_COMPILE_673K".

"Small Molecule" contains electronic energy of N_2, H_2, NH_3 calculated using VASP, PBE and PBE-D3 functionals, and free energy corrections calculated from Jaguar. Free energy corrections include zero point energy (ZPE), Enthalpy, and Entropy (see Column D-G). These energies are raw output from Jaguar. ZPE and Enthalpy are in the unit of Kcal/mol, and entropy is in the unit of cal/mol. For details of rotational, translational and vibrational contributions of each section, user can refer to Row 1-27. Pressure dependence is added by assuming ideal gas, using RT*ln(P2/P1). User can choose any pressure they like by adjusting Column C. "ENERGY_COMPILE_673K" and "ENERGY_COMPILE_730K" will automatically reflect the pressure preference.

"Reaction_Barriers" contains NEB electronic energy of important reaction barriers and along the pathway we purposed in the text. For hydrogenation step and N_2 dissociation step, we used NEB climb to find transition state, if more than one negative frequencies are found, we used dimer method to pinpoint the real transition state. Please refer to Column A-C and picture illustrations within the sheet for NEB energy potential curve. We used electronic adsorption energy+ZPE, for desorption and adsorption barriers for NH_3 and N_2, and please refer to column K-T for them.

User can opt to switch between 673 K and 730 K by selecting and linking the appropriate rows in "Small Molecule" and "Reaction_Barriers". User can select any pressure according to their need, by typing in the pressure in column C of "Small Molecule", in the unit of atm.

5.3 Example

Currently "ENERGY_COMPILE_673K" reflects Somorjai experiment condition: 15 atm pressure for H_2, 5 atm for N_2 and 1.5 torr for NH_3, and here's a screen print of the intermediate and small molecules' energy.

G	H	I	J	K	L	M	N	O	P
	PBE	PBE	PBE	PBE_D3_2.807	PBE_D3_2.807	PBE_D3_2.807	PBE_D3_2.881	PBE_D3_2.881	PBE_D3_2.881
Name	E(tot)	G	dG	E(tot)	G	dG	E(tot)	G	dG
H2(673K,15atm)	**-6.76**	-7.20		**-6.77**	-7.22			-7.22	
N2(673K,5atm)	**-16.60**	-17.66		**-16.65**	-17.71			-17.71	
NH3(673K,1.5 torr)	**-19.52**	-20.25	-1.25	**-19.54**	-20.29	-1.22		-19.94	-0.51
3N.NH2	**-224.10**	-224.34	0.00	-230.00	-231.40	0.00	-229.92	-230.19	0.00
3N.NH2.2H	-230.91	-230.80	0.73	-237.03	-238.05	0.57	-237.02	-236.95	0.46
TS_3N.NH2.2H	-230.09	-230.06	1.47	-236.05	-237.15	1.47			N/A
3N.NH3.H	-231.24	-231.17	0.36	-237.29	-238.32	0.30			N/A
TS_NH3desorption	(Ead = 0.63)	-0.10 from ZPE'	0.89	(Ead = 0.925)	-0.10 from ZPE'	1.12			N/A
3N.H+NH3(g)	-211.10	-211.70	-0.41	-216.82	-218.59	-0.26			N/A
TS_3N.H+NH3(g)	-210.24	-210.75	0.54	-215.79	-217.67	0.66			N/A
2N.NH_diagonal+NH3(g)	-210.76	-211.22	0.07	-216.39	-218.11	0.22			N/A
2N.NH.2H+NH3(g)	-218.10	-218.23	0.25	-223.91	-225.24	0.30			N/A
TS_2N.2H.NH+NH3(g)	-217.53	-217.93	0.56	-223.48	-224.99	0.56			N/A
2N_diagonal.NH2.H+NH3(g)	-218.68	-218.78	-0.29	-224.53	-225.94	-0.39			N/A
TS_2N_diagonal.H.NH2+NH3(g)	-217.09	-217.23	1.26	-222.84	-224.18	1.36			N/A
2N_diagonal.NH3+NH3(g)	-218.20	-218.32	0.17	-223.84	-225.16	0.39	-223.90	-223.91	0.78
TS_NH3desorption	(Ead = 0.88)	-0.10 from ZPE'	0.95	(Ead =1.111)	-0.10 from ZPE'	1.40	(Ead = 1.10)		1.88
2N_diagonal+2NH3(g)	-197.81	-198.51	-0.27	-203.21	-205.14	0.11	-203.28	-203.96	0.79
2N.N2(v.diagonal)+2NH3(g)	-214.86	-215.85	0.05	-220.64	-222.76	0.20			N/A

If the user is curious at energy landscape of high pressure condition, say 150 atm pressure for H_2, 50 atm for N_2 and 1 atm for NH_3, the user need to go to column C of "Small Molecule" and the notation in "ENERGY_COMPILE_673K". Sheet "ENERGY_COMPILE_673K" will automatically reflect the change.

Here's a screen print of the intermediate and small molecules' energy at 150 atm pressure for H_2, 50 atm for N_2 and 1 atm for NH_3.

G	H	I	J	K	L	M	N	O	P
	PBE	PBE	PBE	PBE_D3_2.807	PBE_D3_2.807	PBE_D3_2.807	PBE_D3_2.881	PBE_D3_2.881	PBE_D3_2.881
Name	E(tot)	G	dG	E(tot)	G	dG	E(tot)	G	dG
H2(673K,150atm)	**-6.76**	-7.06		**-6.77**	-7.08			-7.08	
N2(673K,50atm)	**-16.60**	-17.52		**-16.65**	-17.57			-17.57	
NH3(673K,1 atm)	**-19.52**	-19.88	-1.06	**-19.54**	-19.94	-1.05		-19.94	-1.05
3N.NH2	**-224.10**	-224.34	0.00	-230.00	-231.40	0.00	-229.92	-230.19	0.00
3N.NH2.2H	-230.91	-230.80	0.60	-237.03	-238.05	0.43	-237.02	-236.95	0.33
TS_3N.NH2.2H	-230.09	-230.06	1.34	-236.05	-237.15	1.34			N/A
3N.NH3.H	-231.24	-231.17	0.23	-237.29	-238.32	0.16			N/A
TS_NH3desorption	(Ead = 0.63)	-0.10 from ZPE'	0.76	(Ead = 0.925)	-0.10 from ZPE'	0.99			N/A
3N.H+NH3(g)	-211.10	-211.70	-0.18	-216.82	-218.59	-0.04			N/A
TS_3N.H+NH3(g)	-210.24	-210.75	0.76	-215.79	-217.67	0.88			N/A
2N.NH_diagonal+NH3(g)	-210.76	-211.22	0.30	-216.39	-218.11	0.44			N/A
2N.NH.2H+NH3(g)	-218.10	-218.23	0.35	-223.91	-225.24	0.39			N/A
TS_2N.2H.NH+NH3(g)	-217.53	-217.93	0.65	-223.48	-224.99	0.64			N/A
2N_diagonal.NH2.H+NH3(g)	-218.68	-218.78	-0.20	-224.53	-225.94	-0.30			N/A
TS_2N_diagonal.H.NH2+NH3(g)	-217.09	-217.23	1.35	-222.84	-224.18	1.45			N/A
2N_diagonal.NH3+NH3(g)	-218.20	-218.32	0.26	-223.84	-225.16	0.47	-223.90	-223.91	0.51
TS_NH3desorption	(Ead = 0.88)	-0.10 from ZPE'	1.04	(Ead =1.111)	-0.10 from ZPE'	1.49	(Ead = 1.10)		1.61
2N_diagonal+2NH3(g)	-197.81	-198.51	0.19	-203.21	-205.14	0.55	-203.28	-203.96	0.52
2N.N2(v.diagonal)+2NH3(g)	-214.86	-215.85	0.37	-220.64	-222.76	0.51			N/A

5.4 How to obtain rates to be used in the kMC simulations

As discussed in the main text, we evaluated forward and backward rates connecting two different states using transition state theory as $(k_BT/h)\exp(-\Delta G\dagger/k_BT)$, where k_B is the Boltzmann constant, T is the temperature, h is the Planck constant, $\Delta G\dagger$ is the difference in free energy between the starting state and the saddle point. In the case of ER reactions involving gas-phase species turning into adsorbates, we again use transition state theory, but for the reverse desorption process, and then we invoke microscopic reversibility principle to calculate the rate of the direct process.